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EFFECT OF MOLECULAR WEIGHT ON ADHESIVE PROPERTIES OF THE PHENYLETHYNYL-TERMINATED POLYIMIDE LARC™-PETI-5

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INTRODUCTION

Future civilian aircraft will require the use of advanced adhesive systems with high temperature capabilities. One such material has been developed at the NASA Langley Research Center, a phenylethynyl-terminated polyimide given the designation LARC™-PETI-5.[1,2] Recent work has shown the advantages of similar phenylethynyl-terminated polyimides as films, moldings, adhesives, and composite matrix resins.[3-8] Phenylethynyl-terminated oligomers provide greater processing windows than materials which incorporate simple ethynyl endcaps. Since these low molecular weight, low melt viscosity oligomers thermally cure without the evolution of volatile by-products, they provide an excellent means of producing polymers with high glass transition temperatures, excellent solvent resistance, and high mechanical properties.

Three different versions of LARC™-PETI-5 with theoretical number average molecular weights (M_ns) of 2500, 5000, and 10000 g/mol were synthesized in this work. Differential Scanning Calorimetry (DSC) measurements were performed on the dry powder form of these materials to establish cure conditions which result in high glass transition temperatures (T_gs). Lap shear specimens were prepared from adhesive tape made from each material and with the thermal cure conditions determined from the DSC data. The tensile shear data established processing conditions which provided the best adhesive strengths. Further testing was performed to establish the properties of LARC™-PETI-5 as an adhesive material and to determine its solvent resistance.

EXPERIMENTAL

Polymer Synthesis

The three different molecular weight oligomers were prepared as previously reported [1,2] by offsetting the monomer ratio (Table 1) in favor of the diamines and endcapping with the appropriate amount of 4-phenylethynyl phthalic anhydride (Equation 1).

Characterization

Inherent viscosities were measured at 25°C on 0.5% solutions in N-methylpyrrolidinone (NMP). DSC was performed on a Shimadzu DSC-50 calorimeter at a heating rate of 20°C/min with the T_g taken at the inflection point in the heat flow vs. temperature curve.

Adhesive Specimens

Oligomer solutions (15-20% solids in NMP) were used to coat 112 E-glass (A-1100 finish). Each coat was dried in a circulating air oven for one hour each at 100 and 225°C to provide adhesive tapes with volatile contents of ~1-2 %. Twelve to fifteen mil thick tape was produced by applying several coats of the solution. Titanium (Ti-6Al-4v) treated with Pasa-Jell 107™ surface treatment was bonded under varying conditions of temperature and pressure. Four tensile shear specimens of each material type for each condition were tested at either room temperature (RT) or 177°C according to ASTM-1002.

RESULTS AND DISCUSSION

Powdered versions of the 2500, 5000, and 10000 g/mol molecular weight materials cured at various conditions were subjected to DSC analysis to determine T_g. The cure conditions evaluated and the corresponding T_gs are shown in Table 2. All three materials showed the similar results of increasing T_gs with increasing cure temperature. Since all three materials produced similar T_gs, the 5000 g/mol material was chosen to perform further analysis. As shown in Table 3, a T_g as high as 274°C was determined for this material cured for 1/2 hr at 325 and 1/2 hr at 375°C. The results also indicate that a hold at 375°C is required since the ramp to 375°C with no hold produced a T_g

of only 234°C. A processing temperature as low as 316°C resulted in a T_g of 263°C when held for 2 hours. Several cure conditions produced T_gs in a similar range. Four cure conditions were then chosen to make Ti lap shear specimens to evaluate their adhesive properties.

The results from the Ti tensile shear tests are presented in Table 4. As shown by the results, the highest tensile shear strengths were obtained by different processing condition for each material. For the low molecular weight version, a low processing temperature of 316°C for two hours provided the best adhesive properties. The tensile shear results for the 10000 g/mol material were all low, which indicated the need for increased pressure. As evidence by the results is Table 5, increased pressure provides higher strengths for the 10000 g/mol material while pressures as low as 25 psi provide good strengths for the 2500 g/mol material. Overall, excellent adhesive properties were obtained with each of these materials.

These materials also showed excellent solvent resistance. As shown in Table 6, all three materials were essentially unaffected (strength retention between 92 and 100%) by a 48 hour hydraulic fluid soak.

CONCLUSIONS

LARC™-PETI-5 displays excellent adhesive properties. Ti tensile shear strengths as high as 7630 psi at RT and 5100 psi at 177°C were determined. Processing temperatures as low as 316°C and pressures as low as 25 psi resulted in good adhesive properties. The tensile shear properties of these materials are also unaffected by hydraulic fluid. The molecular weight of LARC™-PETI-5 has an important effect on the bonding pressures required to obtain good tensile shear strengths.

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Table 1. Theoretical Molecular Weights, Inherent Viscosities, and Monomer Offset Ratios for Three Molecular Weight Versions of PETI-5.

Theoretical Molecular Weight	Inherent Viscosity, dL/g	Monomer Offset Ratio
2500 g/mole	0.22	0.8276
5000 g/mole	0.38	0.9098
10000 g/mole	0.44	0.9539

Table 2. Glass Transition Temperatures for Three Molecular Weight Versions of PETI-5.

PETI-5, 2500g/mol	**Glass Transition Temp., °C**
Cure Condition	
1 hr @ 300	219
1 hr @ 325	253
1 hr @ 350	254
1 hr @ 375	275
PETI-5, 5000g/mol	**Glass Transition Temp.,°C**
Cure Condition	
1 hr @ 300	239
1 hr @ 325	257
1 hr @ 350	263
1 hr @ 375	270
PETI-5, 10000g/mol	**Glass Transition Temp., °C**
Cure Condition	
1 hr @ 300	258
1 hr @ 325	259
1 hr @ 350	266
1 hr @ 375	271

Table 3. Tgs of PETI-5, 5000 g/mol After Several Cure Conditions.

Cure Condition	Glass Transition Temperature, °C
1 hr @ 300°C	239
1 hr @ 325°C	257
1 hr @ 350°C	263
1 hr @ 375°C	270
1/2 hr @ 375°C	268
1/4 hr @ 375	262
Ramp to 375°C, no hold	234
1/2 hr @ 350°C, 1/2 hr @ 375°C	272
1/2 hr @ 325°C, 1/2 hr @ 375°C	274
2 hr @ 316°C	263

Table 4. Tensile Shear Strengths for PETI-5 at RT and 177°C for Various Cure Temperatures Bonded at 75 psi.

PETI-5, 2500g/mol	**Tensile Shear Strength ,psi**	
Cure Condition	RT	177°C
1 hr @ 350	5470	4520
1 hr @ 375	5760	4330
1/2 hr @ 325, 1/2 hr @ 375	6490	4720
2 hr @ 316	6460	5100
PETI-5, 5000g/mol	**Tensile Shear Strength ,psi**	
Cure Condition	RT	177°C
1 hr @ 350	7630	5000
1 hr @ 375	5290	3840
1/2 hr @ 325, 1/2 hr @ 375	6370	3710
2 hr @ 316	5130	4970
PETI-5, 10000g/mol	**Tensile Shear Strength , psi**	
Cure Condition	RT	177°C
1 hr @ 350	4260	2840
1 hr @ 375	N/A	3160
1/2 hr @ 325, 1/2 hr @ 375	4260	3050
2 hr @ 316	4250	3830

Table 5. Effects of Processing Pressure on Tensile Shear Strength Bonded at 350°C for 1 Hour.

Material	Processing Pressure, psi	Tensile Shear Strength, psi
PETI-5, 2500 g/mol	75	5470
	25	6030
PETI-5, 10000 g/mol	75	4260
	100	6350
	200	6380

Table 6. Tensile Shear Strength After 48 Hour Soak in Hydraulic Fluid With Bonding Conditions of 75 psi, and 350°C for 1 Hour.

Material	Tensile Shear Strength, psi	Strength Retention, %
PETI-5, 2500 g/mol	5430	99
PETI-5, 5000 g/mol	6990	92
PETI-5, 10000 g/mol	4260	100

Equation 1. Polymer Synthesis of PETI-5.